

Form PTO-1390 (Rev. 12-29-99)		US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NO <b>M 6726 PCT/US</b>	
<b>TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371</b>				U.S. APPLICATION NO. (if known file 37 CFR 1.51) <div style="font-size: 1.5em; font-weight: bold;">10/088058</div>	
INTERNATIONAL APPLICATION NO <b>PCT/US/00/24930</b>		INTERNATIONAL FILING DATE <b>September 12, 2000</b>		PRIORITY DATE CLAIMED <b>September 13, 1999</b>	
TITLE OF INVENTION <b>PRE-PAINT TREATMENT OF METAL AND PRODUCT THEREOF</b>					
APPLICANT(S) FOR DO/EO/US Yasuhiro Kinoshita, Kensuke Mizuno and Katsuyuki Kawakami					
Applicant herewith submits to the United States Designated/Elected Office (EO/DO/US) the following items and other information:					
<ol style="list-style-type: none"> <li>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371</li> <li>3. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1)</li> <li>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</li> <li>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)).           <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau)</li> <li>b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li>6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</li> <li>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))           <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau)</li> <li>b. <input type="checkbox"/> have been transmitted by the International Bureau</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired</li> <li>d. <input checked="" type="checkbox"/> have not been made and will not be made</li> </ol> </li> <li>8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)) (unexecuted)</li> <li>10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5))</li> </ol>					
<b>Items 11. to 16. below concern other document(s) or information included:</b>					
<ol style="list-style-type: none"> <li>11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98</li> <li>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included</li> <li>13. <input checked="" type="checkbox"/> A FIRST preliminary amendment  <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment</li> <li>14. <input type="checkbox"/> A substitute specification</li> <li>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li>16. <input checked="" type="checkbox"/> Other items or information              idc with references           </li> </ol>					
"Express Mail" mailing label number <u>EL615775321US</u>					

U.S. Application No (If known, see 37 CFR 1.5) <div style="font-size: 1.5em; font-weight: bold; margin-left: 100px;">10/088058</div>		INTERNATIONAL APPLICATION NO. <b>PCT/US00/24930</b>		ATTORNEY'S DOCKET NUMBER <b>M 6726 PCT/US</b>	
17. <input type="checkbox"/> The following fees are submitted: <b>BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):</b> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO..... <b>\$1,040.00</b>  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO..... <b>\$890.00</b>  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37CFR 1.445(a)(2)) paid to USPTO ..... <b>\$740.00</b>  International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... <b>\$710.00</b>  International preliminary examination fee paid to USPTO (37CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4)..... <b>\$100.00</b>  <div style="text-align: right;"><b>ENTER APPROPRIATE BASIC FEE AMOUNT</b>      =</div>				<div style="display: flex; justify-content: space-between; font-size: 0.8em;"> <span>CALCULATIONS</span> <span>PTO USE ONLY</span> </div> <div style="border-top: 1px solid black; border-bottom: 1px solid black; height: 20px; margin-top: 10px;"></div>	
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date 37 (CFR 1.492(e)).				<div style="border-top: 1px solid black; border-bottom: 1px solid black; height: 20px; margin-top: 10px;"></div>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	12 - 20 =	0	0 X \$18.00	\$ 0	
Independent Claims	1 - 3 =	0	0 X \$84.00	\$ 0	
Multiple dependent claims (s)(if applicable)      0			+ \$280.00	\$ 0	
<b>TOTAL OF ABOVE CALCULATIONS</b> =				\$ 0	
Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				<div style="border-top: 1px solid black; border-bottom: 1px solid black; height: 20px; margin-top: 10px;"></div>	
<b>SUBTOTAL</b> =				\$ 740	
Processing fee of <b>\$130.00</b> for furnishing the English translation later the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				<div style="border-top: 1px solid black; border-bottom: 1px solid black; height: 20px; margin-top: 10px;"></div>	
<b>TOTAL NATIONAL FEE</b> =				\$ 740	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				<div style="border-top: 1px solid black; border-bottom: 1px solid black; height: 20px; margin-top: 10px;"></div>	
<b>TOTAL FEES ENCLOSED</b> =				\$ 740	
				Amount to be: refunded:	\$-----
				charged:	<b>\$ 740.00</b>
a. <input type="checkbox"/> A check in the amount of \$ _____ to cover the above fees is enclosed.  b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>01-1250</u> in the amount of <b>\$740.00</b> to cover the above fees. A triplicate copy of this sheet is enclosed. Order No. <u>02-0121</u> . c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>01-1250</u> . A duplicate copy of this sheet is enclosed. <b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b))</b> <b>must be filed and granted to restore the application to pending status.</b>					
SEND ALL CORRESPONDENCE TO:    Henkel Corporation, Law Dept. 2500 Renaissance Blvd., Suite 200 Gulph Mills, PA 19406			<div style="text-align: center;">           SIGNATURE:       </div> <div style="margin-top: 10px;">         Stephen D. Harper          NAME ATTORNEY FOR APPLICANT          33,243          REGISTRATION NUMBER       </div>		

"Express Mail" mailing label number 4615-72532/US Date of Deposit 3-13-02

PATENT

Docket No. M 6726 PCT/US

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

RE: PCT/US/00/24930  
International Filing Date: September 12, 2000  
Priority Date Claimed: September 13, 1999  
Applicant: Kinoshita et al.  
Title: PRE-PAINT TREATMENT OF METAL AND PRODUCT THEREOF

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Box PCT  
Washington, DC 20231

ATTN: DO/EO/US

Sir:

Prior to substantive examination of the above-referenced application, please enter the following amendment.

**IN THE SPECIFICATION:**

Insert the following new paragraph beginning on a new line on page 1 immediately following the title:

This application claims priority from International Application No. PCT/US00/24930, filed September 12, 2000, and published in English, and Japanese application H11-258,309, filed September 13, 1999.

Amend the paragraph beginning at line 11 on page 2 to read as follows:

It has been discovered that a coating film possessing not only corrosion resistance but also superior adhesion can be formed by treating the surface of a metal material with an aqueous treatment agent that contains a specified resin, a silane coupling agent and fine particles with a particle size of 1.0 micrometer (hereinafter usually abbreviated as "µm") or smaller. This discovery led to the present invention.

Amend the paragraph beginning at line 22 on page 4 to read as follows:

The non-volatiles content of component (b) preferably is at least, with increasing preference in the order given, 15, 18, 20, 22, or 24 percent by weight and independently

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preferably is not greater than, with increasing preference in the order given, 50, 40, 38, or 36 percent by weight of the total non-volatiles content. If the non-volatiles content of component (b) is less than 20 percent by weight relative to 100 percent by weight of the total non-volatiles content, the adhesion of the coating film drops, as is undesirable.

On the other hand, if the non-volatiles content of component (b) exceeds 60 percent by weight, the relative proportion of component (a) in the coating film drops, so that the corrosion resistance drops, as is also undesirable. Good practical results are facilitated by a concentration within the more preferred ranges.

Amend the paragraph beginning at line 32 on page 4 to read as follows:

Component (c) is selected from the group consisting of plastic pigments, phosphorus-containing anti-rust pigments, and colloidal-sized silica (including fumed silica), alumina, zirconia, and titania. It is more preferable if any silica, alumina, zirconia, or titania used for component (c) has in fact been prepared as stable colloid dispersed in a fluid continuous phase. If the mean particle size of component (c) exceeds 1.0  $\mu\text{m}$ , some of the particles are likely to protrude from the surface of the coating film; as a result, moisture may easily invade the surface of the material from the particle interfaces, thus causing a drop in corrosion resistance and adhesion. Accordingly, such a large mean particle size is undesirable.

Amend line 1 on page 20 to read as follows:

What is claimed is:

IN THE CLAIMS:

Amend claims 1, 2 and 9 to read as follows:

1. (Amended) An aqueous liquid composition of matter suitable for treating a metal substrate comprising water and the following components:
  - (a) from 20 to 70 percent by weight of non-volatile constituents of a component selected from a group consisting of urethane resins, epoxy resins, and acrylic resins;
  - (b) from 10 to 60 percent by weight of non-volatile constituents of a component of

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silane coupling agent; and

- (c) from 10 to 40 percent by weight of a component of dispersed solid non-volatile particles with a mean particle size of 1.0  $\mu\text{m}$  or less,

all of the percentage values specified above for components (a), (b), and (c) being percentages of only the non-volatiles content of said aqueous liquid composition.

2. (Amended) A liquid composition according to claim 1, wherein component (c) is selected from the group consisting of plastic pigments, phosphorus-containing anti-rust pigments, and colloidal-sized silica, alumina, zirconia, and titania.

9. (Amended) An article of manufacture comprising a coated metal surface formed by a process according to claim 5.

Enter the following new claims 10-12:

10. (New) An aqueous liquid composition of matter comprising water and the following components:

- (a) from 30 to 60 percent by weight of non-volatile constituents of a component selected from a group consisting of urethane resins, epoxy resins, and acrylic resins;
- (b) from 22 to 38 percent by weight of non-volatile constituents of a component of silane coupling agent; and
- (c) from 10 to 35 percent by weight of a component of dispersed solid non-volatile particles with a mean particle size of 1.0  $\mu\text{m}$  or less, said particles being selected from the group consisting of plastic pigments, phosphorus-containing anti-rust pigments and colloidal-sized silica, alumina, zirconia, and titania, all of the percentage values specified above for components (a), (b), and (c) being percentages of only the non-volatiles content of said aqueous liquid composition and said aqueous liquid composition having a pH in a range from 2 to 10.

11. (New) A process for making a coated metal substrate, said process comprising operations of:

- (I) forming a layer of a liquid composition according to claim 10 over at least one of a metallic surface of said metal substrate, a surface formed by chemical plating

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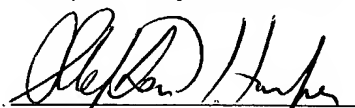
- on a metallic surface of said metal substrate, and a phosphate conversion coating formed on a metallic surface of said metal substrate, said layer of said liquid composition having a non-volatiles content that is from 0.05 to 0.5 g/m<sup>2</sup>; and
- (II) drying said layer of liquid composition, without removing any of said liquid by any other method than volatilization, to form a dry coating.
12. (New) The process of claim 11 wherein said metal substrate reaches a peak temperature during step 11 of from 50 to 250°C.

**REMARKS**

The specification has been amended to include a claim to priority of earlier-filed International and Japanese applications.

The specification has also been amended to correct certain inadvertent typographical errors which appear in the paragraphs beginning at line 11 on page 2 and at line 32 on page 4 and the paragraph beginning at line 22 on page 4. Support for the former amendments may be found on page 2, line 25, of the specification as well as in Claim 1 and in the Abstract of the Disclosure. Support for the latter amendment is found in the paragraph as originally filed, wherein it is clear that the phrase "50, 40, 38 or 36 percent by weight" was intended by the Applicants to refer to the preferred maximum levels of the non-volatiles content of component (b) which are present in the aqueous treatment agent composition and not the preferred minimum levels.

Respectfully submitted,



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**Preliminary Amendment of U.S. National Stage for International Application  
PCT/US00/24930 filed September 12, 2000**

Version Marked to Show Changes Made

**IN THE SPECIFICATION:**

The paragraph beginning at line 11 on page 2 has been amended as follows:

It has been discovered that a coating film possessing not only corrosion resistance but also superior adhesion can be formed by treating the surface of a metal material with an aqueous treatment agent that contains a specified resin, a silane coupling agent and fine particles with a particle size of 1.0 [millimeter] micrometer (hereinafter usually abbreviated as ["mm"] "μm") or smaller. This discovery led to the present invention.

The paragraph beginning at line 22 on page 4 has been amended as follows:

The non-volatiles content of component (b) preferably is at least, with increasing preference in the order given, 15, 18, 20, 22, or 24 percent by weight and independently preferably is [at least] not greater than, with increasing preference in the order given, 50, 40, 38, or 36 percent by weight of the total non-volatiles content. If the non-volatiles content of component (b) is less than 20 percent by weight relative to 100 percent by weight of the total non-volatiles content, the adhesion of the coating film drops, as is undesirable. On the other hand, if the non-volatiles content of component (b) exceeds 60 percent by weight, the relative proportion of component (a) in the coating film drops, so that the corrosion resistance drops, as is also undesirable. Good practical results are facilitated by a concentration within the more preferred ranges.

The paragraph beginning at line 32 on page 4 has been amended as follows:

Component (c) is selected from the group consisting of plastic pigments, phosphorus-containing anti-rust pigments, and colloidal-sized silica (including fumed silica), alumina, zirconia, and titania. It is more preferable if any silica, alumina, zirconia, or titania used for component (c) has in fact been prepared as stable colloid dispersed in a fluid continuous phase. If the mean particle size of component (c)

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exceeds 1.0 [mm]  $\mu\text{m}$ , some of the particles are likely to protrude from the surface of the coating film; as a result, moisture may easily invade the surface of the material from the particle interfaces, thus causing a drop in corrosion resistance and adhesion. Accordingly, such a large mean particle size is undesirable.

**IN THE CLAIMS**

Claims 1, 2 and 9 have been amended as follows:

1. (Amended) An aqueous liquid composition of matter suitable for treating a metal substrate[, either directly or after formation of a chemical plating layer or a phosphate conversion coating layer over said metal substrate, to form over the substrate a corrosion protective layer with excellent adhesion to subsequent paint coatings, said aqueous liquid composition] comprising water and the following components:
  - (a) from 20 to 70 percent by weight of non-volatile constituents of a component selected from a group consisting of urethane resins, epoxy resins, and acrylic resins;
  - (b) from 10 to 60 percent by weight of non-volatile constituents of a component of silane coupling agent; and
  - (c) from 10 to 40 percent by weight of a component of dispersed solid non-volatile particles with a mean particle size of 1.0  $\mu\text{m}$  or less,
 all of the percentage values specified above for components (a), (b), and (c) being percentages of only the non-volatiles content of said aqueous liquid composition.
2. (Amended) A liquid composition according to claim 1, wherein component (c) is selected from the group consisting of plastic pigments, phosphorus-containing anti-rust pigments, and colloidal-sized silica [(including fumed silica)], alumina, zirconia, and titania.
9. (Amended) An article of manufacture comprising a coated metal surface formed by a process according to [any one of claims] claim 5 [through 8].



10/088058

Rec'd PCT/PTO 13 MAR 2002

DescriptionPRE-PAINT TREATMENT OF METAL AND PRODUCT THEREOF

## FIELD AND BACKGROUND OF THE INVENTION

The present invention relates to a pre-paint aqueous treatment agent which is used to make functionally surface treated steel sheets that are variously known as "colored", "painted", or "PCM" steel sheets, a process for manufacturing such a functionally surface treated metal material with superior adhesion using this pre-paint aqueous treatment agent, and a metal material so made.

Functionally surface treated steel sheets are used in household electrical appliances, construction materials, automobiles, etc. Such steel sheets are covered with an organic coating film after the metal substrate has been subjected to a chromate conversion coating treatment; accordingly, such plates have superior design properties in addition to superior workability and corrosion resistance. However, as concern for the protection of the global environment has increased in recent years, the movement to avoid the use of substances harmful to the human body (in the case of colored steel sheets, hexavalent chromium contained in the undersurface and organic coating film) has become stronger. Recently, therefore, there has been an increased demand for chromium-free (non-chromate type) undersurface treatment agents and chromium-free (non-chromate type) organic coating film agents.

Conventional techniques relating to such agents are disclosed in Japanese Patent Application Kokai No. 59-116381 and Japanese Patent Application Kokai No. 4-66173, etc. The technique disclosed in Japanese Patent Application Kokai No. 59-116381 is a process in which zinc and zinc alloy surfaces are treated with an aqueous solution that contains tannic acid and a silane coupling agent, and a coating film is formed on these surfaces. However, since tannic acid is soluble in water, the adhesion that is the goal of this invention cannot be obtained in the case of coating films produced by this process. The technique disclosed in Japanese Patent Application Kokai No. 4-66173 relates to metal sheets in which the surfaces of aluminum-plated metal sheets or aluminum plates are coated with a treatment solution whose essential components are one or more compounds selected from a set consisting of fluorine compounds of titanium or zirconium, and one or more agents selected from a group consisting of silane coupling agents that have amino groups, epoxy groups or mercapto groups, after which this coating is dried and a heat-resistant resin containing sulfur atoms is formed on top of this coating. The metal sheets obtained by this process have a superior heat resistance; however, the adhesion that is the goal of this invention cannot be obtained.

Thus, under current conditions, conversion coating films with superior corrosion resistance and adhesion which can be used as pre-paint undersurfaces instead of chromate conversion coating films cannot be obtained using any process known to the applicants.

Major objects of the present invention are to provide a pre-paint aqueous treatment agent which can form a coating film that has superior corrosion resistance and paint adhesion properties on the surface of a metal material, a process for manufacturing a metal substrate coated using this pre-paint aqueous treatment agent, and an article of manufacture including such a coated metal material substrate.

#### BRIEF SUMMARY OF THE INVENTION

It has been discovered that a coating film possessing not only corrosion resistance but also superior adhesion can be formed by treating the surface of a metal material with an aqueous treatment agent that contains a specified resin, a silane coupling agent and fine particles with a particle size of 1.0 millimeter (hereinafter usually abbreviated as "mm") or smaller. This discovery led to the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

Specifically, the pre-paint aqueous liquid treatment agent of the present invention, which has superior adhesion, is characterized by the fact that said agent comprises, preferably consists essentially of, or more preferably consists of, water and the following components:

- (a) from 20 to 70 percent by weight of a component selected from a group consisting of urethane resins, epoxy resins, and acrylic resins;
- (b) from 10 to 60 percent by weight of a component of silane coupling agent; and
- (c) from 10 to 40 percent by weight of a component of dispersed solid particles with a mean particle size of 1.0  $\mu\text{m}$  or less,

all of the percentage values specified above for components (a), (b), and (c) being percentage of the non-volatiles content of the treatment agent only.

In a process of the present invention, at least one surface of a metal substrate, which may optionally have been previously subjected to a chemical plating treatment or a phosphate conversion coating treatment is coated with a liquid layer of the aforementioned pre-paint aqueous treatment agent, and later, usually preferably more or less immediately after the liquid coating layer has been formed, the liquid coating is dried, without any of the non-volatile content of the liquid layer having been removed by any method other than volatilization, e.g., by rinsing with another liquid. A dry coating film thus formed preferably has a mass per unit area coated, a value often referred to as "coating weight", that is from 0.05 to 1.0 grams of dry coating per square meter of





ceeds 1.0 mm, some of the particles are likely to protrude from the surface of the coating film; as a result, moisture may easily invade the surface of the material from the particle interfaces, thus causing a drop in corrosion resistance and adhesion. Accordingly, such a large mean particle size is undesirable.

5 Examples of commercially available fine particles with a mean particle size of 1.0  $\mu\text{m}$  or less that are suitable for component (c) include the following: SNOWTEX 20, 30, 40, 50, C, N, O, S, 20L, L, UP, OUP, XL, YL, ZL, P-1040, MP-3040, MP-4540, AK, and BK and QAS 40 and 25 colloidal dispersions of silica in water, all manufactured by Nissan Kagaku Kogyo K.K.; AEROSIL 130, 200, 300, 380, TT600, MOX80, and MOX170  
10 fumed silicas manufactured by Nippon Aerosil K.K.; ALUMINA-SOL 100, 200, 520 dispersions of alumina in water manufactured by Nissan Kagaku Kogyo K.K.; NZS -20A, -30A, and -30B dispersions of zirconia in water manufactured by Nissan Kagaku Kogyo K.K.; pulverized zinc phosphate, aluminum phosphate, and calcium phosphate as examples of phosphorus-containing rust-inhibiting pigments; and MUTICLE 100P and  
15 240D plastic pigments manufactured by Mitsui Kagaku K.K., ROPAQUE OP-62 and HP-91 plastic pigments manufactured by Rohm and Haas Co., and MP-1000, -1100, -1201, -1450, -1451, -1600, -2701, -3100, and -4009 plastic pigments manufactured by Soken Kagaku K.K. Furthermore, component (c) may also consist of a mixture of two or more types of particles.

20 The solids content of component (c) preferably is from 10 to 35 percent by weight, or more preferably 10 to 30 percent by weight, relative to 100 percent by weight of the total non-volatiles content of the aqueous liquid treatment. (Because component (c) is defined to be dispersed solids, its solids content is the same as its non-volatiles content.) If the solids content of component (c) is less than 10 percent by weight relative  
25 to 100 percent by weight of the total non-volatiles content, the adhesion drops. Accordingly, such a small solids content is undesirable. On the other hand, if the solids content of component (c) exceeds 40 percent by weight, the coating film becomes hard and brittle so that the corrosion resistance and adhesion drop. Accordingly, such a large solids content is also undesirable.

30 The pH of the pre-paint aqueous treatment agent of the present invention is preferably in the range of 2 to 10, and is even more preferably in the range of 2.5 to 9.5. If the pH of the treatment agent is less than 2, there is a danger that the metal substrate will be etched and that the corrosion resistance will drop. Accordingly, such a low pH is undesirable. On the other hand, if the pH exceeds 10, the alkali component remaining  
35 in the coating film usually causes a drop in the water resistance. Accordingly, such a high pH is also undesirable. Furthermore, there are no narrow restrictions on the

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The present invention may be further appreciated by consideration of the working examples of the present invention and comparative examples presented below. However, the scope of the present invention is not limited by these working examples.

The test samples, pretreatments and pre-paint aqueous treatment agent coating processes used in the following working examples and comparative examples are described below.

## 1. Preparation of Test Samples

### (1-1) Tested Metal Substrates

The commercially marketed materials indicated below, with short codes used to identify the substrates in a table below following each type in parentheses, were used as test materials:

Melt-galvanized steel sheets ("GI") — Sheet thickness = 0.5 millimeter (hereinafter usually abbreviated as "mm"), coating weight = 90/90 g/m<sup>2</sup>;

Melt-galvanized steel sheets containing 5 % aluminum in the galvanizing coating ("GF") — Sheet thickness = 0.5 mm, coating weight = 90/90 g/m<sup>2</sup>;

Melt-55 %-zinc-45 % aluminum galvanized steel sheets ("GL") — Sheet thickness = 0.8 mm, coating weight = 90/90 g/m<sup>2</sup>;

A-1100 type aluminum plates ("AL") — Sheet thickness = 0.8 mm.

### (1-2) Degreasing Treatment

The test substrates were subjected to a spray treatment for 2.0 minutes at a temperature of 60 °C, using as degreaser a solution in water of FINECLEANER® 4336 alkaline degreasing agent concentrate (commercially available from Nihon Parkerizing Co., Ltd., Tokyo) at a concentration of 20 grams of the concentrate per liter of degreasing agent, this unit of concentration being freely used hereinafter for any constituent of any liquid and being usually abbreviated as "g/l". The test substrates were then washed for 30 seconds with pure water and dried.

### (1-3) Pretreatments

#### (1-3-1) Chemical Plating Treatment

The test substrates which had been subjected to the abovementioned degreasing treatment were subjected to a spray treatment at a concentration of 100 g/l and a temperature of 50 °C, using PREPALENE® 4015 chemical nickel plating liquid (commercially available from Nihon Parkerizing Co., Ltd.). The test substrates were then washed for 30 seconds with deionized water and dried. The amount of adhering nickel was found to be 20 mg/m<sup>2</sup>.

#### (1-3-2) Phosphate Formation Treatment



Test substrates which had been subjected to the abovementioned degreasing treatment were dipped for 10 seconds at a temperature of 30 °C in a solution containing 1.0 g/l in water of PREPALENE® Z surface conditioning agent concentrate (manufactured by Nihon Parkerizing Co., Ltd.). Afterward, the test substrates were subjected to a dipping treatment at a temperature of 60 °C in a solution in water of 60 g/l of PAL-BOND® L3300 phosphate conversion coating agent (manufactured by Nihon Parkerizing Co., Ltd.). The test substrates were then washed for 30 seconds with deionized water and dried. The amount of phosphate conversion coating was 2 g/m<sup>2</sup>.

#### (1-4) Application of Surface Treatment Agents According to the Invention

The pre-paint aqueous treatment agents described below were applied by means of a bar coater, and were dried at a temperature of 300 °C.

### 2. Preparation and Constitution of the Aqueous Pre-Paint Treatment Agents

(Note: All "parts" and percentages stated below are by weight.)

#### Treatment Agent A

Amounts of 100 parts of SUPERFLEX 700 (concentration of non-volatiles content 35 %) urethane resin manufactured by Daiichi Kogyo Seiyaku K.K. to supply component (a), 35 parts of γ-glycidoxypolytriethoxysilane (concentration of non-volatiles content 100 %) manufactured by Toshiba Silicone K.K. to supply component (b), and 150 parts of SNOWTEX 20 (concentration of solids 20 %) colloidal silica dispersion manufactured by Nissan Kagaku Kogyo K.K. to supply component (c) were measured and mixed with 1710 parts of deionized water by means of propeller agitation. The pH of this treatment solution was adjusted to 8 by the dropwise addition of an appropriate amount of a 5 % aqueous solution of ammonia. The part of the total non-volatiles content of the treatment solution that was component (a) was 35 percent, the part of total non-volatiles content of the treatment solution that was component (b) was 35 percent, and the part of total non-volatiles content of the treatment solution that was solids content of component (c) was 30 percent. The concentration of the total non-volatiles content of the treatment solution was 5.0 %.

#### Treatment Agent B

Amounts of 100 parts of EPI REZ 5003W55 (concentration of non-volatiles content 55 %) epoxy resin manufactured by Yuka Shell Epoxy K.K. to supply component (a), 25 parts of N-β-(aminoethyl)-γ-aminopropylmethyldimethoxysilane (concentration of non-volatiles content 100%) manufactured by Toshiba Silicone K.K. to supply component (b), and 100 parts of ZIRCONIA-SOL NZS-20A (concentration of solids content 20%) zirconia sol manufactured by Nissan Kagaku K.K. to supply component (c) were measured out and dispersed in 2275 parts of deionized water by means of propeller agitation. The

pH of this treatment solution was adjusted to 4 by the dropwise addition of an appropriate amount of a 5 % aqueous solution of acetic acid. The weight of the non-volatiles content of component (a) was 55 percent by weight, the weight of the non-volatiles content of component (b) was 25 percent by weight, and the weight of the solids content of component (c) was 20 percent by weight, all relative to 100 percent by weight of the total non-volatiles content of the treatment solution, and the total concentration of the non-volatiles content of the treatment solution was 4 %.

#### Treatment Agent C

Amounts of 100 parts of PRIMALL K-3 (concentration of non-volatiles content 46 %) acrylic resin manufactured by Rohm and Haas Co. to supply component (a), 20 parts of  $\gamma$ -mercaptopropyltrimethoxysilane (concentration of non-volatiles content 100 %) manufactured by Toshiba Silicone K.K. as component (b), and 94 parts of SNOWTEX OUP (concentration of non-volatiles content 15 %) colloidal silica manufactured by Nissan Kagaku Kogyo K.K. to supply component (c) were measured out and dispersed in 2286 parts of deionized water by means of propeller agitation. The pH of this treatment solution was adjusted to 9 by the dropwise addition of an appropriate amount of a 5 % aqueous solution of triethylamine. The weight of the non-volatiles content of component (a) was 58 percent by weight, the weight of the non-volatiles content of component (b) was 25 percent by weight and the weight of the solids content of component (c) was 17 percent by weight, relative to 100 percent by weight of the total non-volatiles content of the treatment solution. The concentration of the total non-volatiles content of the treatment solution was 4 %.

#### Treatment Agent D

Amounts of 80 parts of EPI REZ 5003W55 (concentration of non-volatiles content 55 %) epoxy resin manufactured by Yuka Shell Epoxy K.K. and 60 parts of FINETEX ES-2200 (concentration of non-volatiles content 25 %) epoxy resin manufactured by Dai-Nippon Inki Kagaku Kogyo K.K. to jointly supply component (a), 31 parts of  $\gamma$ -glycidoxypolytriethoxysilane (concentration of non-volatiles content 100 %) manufactured by Toshiba Silicone K.K. to supply component (b), and 100 parts of ALUMINA-SOL 100 (concentration of solids content 10 %) alumina sol manufactured by Nissan Kagaku Kogyo K.K. to supply component (c) were measured out and dispersed in 729 parts of deionized water by means of propeller agitation. The pH of this treatment solution was adjusted to 3 by the dropwise addition of an appropriate amount of a 5 % aqueous solution of phosphoric acid. The weight of the non-volatiles content of component (a) was 59 percent by weight, the weight of the non-volatiles content of component (b) was 31 percent by weight, and the weight of the solids content of component (c) was 10

percent by weight, all relative to the total non-volatiles content of the treatment solution. The concentration of the non-volatiles content of the treatment solution was 10 %.

#### Treatment Agent E

Amounts of 100 parts of PRIMAL K-3 (concentration of non-volatiles content 46  
5 %) acrylic resin manufactured by Rohm and Haas Co. to supply component (a), 10 parts  
of  $\gamma$ -glycidoxypropyltriethoxysilane (concentration of non-volatiles content 100 %) and 10  
parts of  $\gamma$ -chloropropyltrimethoxysilane (concentration of non-volatiles content 100 %) both  
manufactured by Toshiba Silicone K.K. were measured out to supply component  
(b), and 32 parts of MUTICLE 240D (concentration of non-volatiles content 44 %) plastic  
10 pigment manufactured by Mitsui Kagaku K.K. to supply component (c) were measured  
out and dispersed in 1098 parts of deionized water by means of propeller agitation. The  
pH of this treatment solution was adjusted to 8 by the dropwise addition of an appropriate  
amount of 5 % aqueous ammonia. The weight of the non-volatiles content of component  
(a) was 58 percent by weight, the weight of the non-volatiles content of component (b)  
15 was 25 percent by weight and the weight of the non-volatiles content of component (c)  
was 17 percent by weight, relative to 100 percent by weight of the total non-volatiles con-  
tent of the treatment solution. The concentration of the total non-volatiles content of the  
treatment solution was 8 %.

#### Comparative Treatment Agent F

20 Amounts of 35 parts of  $\gamma$ -glycidoxypropyltriethoxysilane (concentration of non-  
volatiles content 100 %) manufactured by Toshiba Silicone K.K. and 150 parts of SNOW-  
TEX 20 (concentration of non-volatiles content 20 %) colloidal silica manufactured by  
Nissan Kagaku Kogyo K.K. were measured out and dispersed in 1115 parts of water by  
means of propeller agitation. The pH of this treatment solution was adjusted to 8 by the  
25 dropwise addition of an appropriate amount of 5 % aqueous ammonia. The concentra-  
tion of the non-volatiles content of this treatment solution was 5 %. This treatment  
solution did not contain any material corresponding to component (a) of a treatment  
composition according to this invention.

#### Comparative Treatment Agent G

30 Amounts of 100 parts of SUPERFLEX 700 (concentration of non-volatiles content  
35 %) urethane resin manufactured by Daiichi Kogyo Seiyaku K.K. and 150 parts of  
SNOWTEX 20 (concentration of non-volatiles content 20 %) colloidal silica manufactured  
by Nissan Kagaku Kogyo K.K. were measured out and dispersed in 1050 parts of de-  
ionized water by means of propeller agitation. The pH of this treatment solution was ad-  
justed to 8 by the dropwise addition of an appropriate amount of 5 % aqueous ammonia.  
35 The concentration of the non-volatiles content of this treatment solution was 5 %. This



were measured out and dispersed in 1714 parts of deionized water by means of propeller agitation. The pH of this treatment solution was adjusted to 8 by the dropwise addition of an appropriate amount of 5 % aqueous ammonia. The concentration of the non-volatiles content of this treatment solution was 5 %. The weight of the non-volatiles content of the material corresponding to component (a) in a composition according to this invention was 14 percent by weight, the weight of the non-volatiles content of the material corresponding to component (b) in a composition according to this invention was 46 percent by weight, and the weight of the non-volatiles content of the material corresponding to component (c) in a composition according to this invention was 40 percent by weight, relative to 100 percent by weight of the total non-volatiles content of the treatment solution. Thus, the weight of the non-volatiles content of component (a) was below the lower limit specified for a composition according to this invention.

#### Comparative Treatment Agent K

Amounts of 200 parts of SUPERFLEX 700 (concentration of non-volatiles content 35 %) urethane resin manufactured by Daiichi Kogyo Seiyaku K.K., 5 parts of  $\gamma$ -glycid-oxypropyltriethoxysilane (concentration of non-volatiles content 100 %) manufactured by Toshiba Silicone K.K., and 125 parts of SNOWTEX 20 (concentration of non-volatiles content 20 %) colloidal silica dispersion manufactured by Nissan Kagaku Kogyo K.K., were measured out and dispersed in 1670 parts of deionized water by means of propeller agitation. The pH of this treatment solution was adjusted to 8 by the dropwise addition of an appropriate amount of 5 % aqueous ammonia. The concentration of the non-volatiles content of this treatment solution was 5 %. The weight of the non-volatiles content of the material corresponding to component (a) in a composition according to this invention was 70 percent by weight, the weight of the non-volatiles content of the material corresponding to component (b) in a composition according to this invention was 5 percent by weight, and the weight of the non-volatiles content of the material corresponding to component (c) in a composition according to this invention was 25 percent by weight, relative to 100 percent by weight of the total non-volatiles content of the treatment solution. Thus, the weight of the non-volatiles content of the material corresponding to component (b) in a composition according to this invention was below the lower limit specified for a composition according to this invention.

#### Comparative Treatment Agent L

Amounts of 60 parts of SUPERFLEX 700 (concentration of non-volatiles content 35 %) urethane resin manufactured by Daiichi Kogyo Seiyaku K.K., 64 parts of  $\gamma$ -glycid-oxypropyltriethoxysilane (concentration of non-volatiles content 100 %) manufactured by Toshiba Silicone K.K., and 75 parts of SNOWTEX 20 (concentration of non-





#### 4.2.1 Primary Folding Adhesion Test

In accordance with the test process described in JIS-G3312, the respective test coated substrates were subjected to a 2T folding test with two spacing sheets inside the fold at 20 °C. An evaluation of the extent of stripping of the coatings from the test coated substrates was performed, following the stripping of the tape over the part of the coated substrate evaluated, and is reported using the following scale:

- ⊙: no stripping
- ⊙ - O: stripped area of less than 10 %
- O: stripped area of 10 % or greater, but less than 50 %
- Δ: stripped area of 50 % or greater, but less than 80 %
- X: stripped area of 80 % or greater.

#### 4.2.2 Secondary Folding Adhesion Test

The test sheets were immersed in boiling water for 2 hours, and were then allowed to stand for one day. Afterward, a test was performed in the same manner as the primary folding adhesion test. The reporting scale was the same as for the primary folding adhesion test.

#### 4.3 Coin Scratching Test

A copper coin approximately the size of a U.S. quarter dollar (a Japanese 10-yen coin) was positioned at an angle of 45 degrees relative to each test sheet, and this coin was rubbed across the coating film at a constant speed under a load of 3 kilograms. The susceptibility of the coating film to scratching was then evaluated and is reported using the following scale:

- ⊙: 0 % exposure of any part of the substrate under the primer
- ⊙ - O: less than 10 % exposure of any part of the substrate under the primer
- O: exposure of 10 % or greater, but less than 50 %, of any part of the substrate under the primer
- Δ: exposure of 50 % or greater, but less than 80 %, of any part of the substrate under the primer
- X: exposure of 80 % or greater of any part of the substrate under the primer.

A summary of the test conditions used for the pre-paint aqueous treatment agents is shown in Table 1, and a summary of the coated sheet performance test results obtained with these pre-paint aqueous treatment agents is shown in Table 2.

Working Examples No. 1 through 13 in Table 1 show the coated sheet performance values for metal materials on which coating films were formed by applying and drying pre-paint aqueous treatment agents of the present invention. It may be seen that the



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corrosion resistance, primary folding adhesion, secondary folding adhesion and coin scratching properties were all good. In Comparative Examples No. 1 through 11 in Table 1, the corrosion resistance, primary folding adhesion, secondary folding adhesion and coin scratching properties were all inferior. Accordingly, the contribution of the present invention to industry is extremely significant.

Table 1

Identifier	Substrate Material	Pretreatment	Treatment Solution Used	Peak Metal Temperature During Drying, °C	Coating Weight, g/m <sup>2</sup>
Example 1	GI	None	A	70	0.4
Example 2	GI	None	B	70	0.4
Example 3	GI	None	C	70	0.4
Example 4	GI	None	D	70	0.4
Example 5	GI	None	E	70	0.4
Example 6	GF	None	A	70	0.4
Example 7	GL	None	B	70	0.4
Example 8	AL	None	C	70	0.4
Example 9	GI	None	D	120	0.4
Example 10	GI	None	E	180	0.4
Example 11	GI	None	A	70	1.0
Example 12	GI	Chemical Plating	A	70	0.1
Example 13	GI	Phosphate Conversion Coating	B	70	0.1
Comparative Example 1	GI	None	F	70	0.4
Comparative Example 2	GI	None	G	70	0.4
Comparative Example 3	GI	None	H	70	0.4
Comparative Example 4	GI	None	I	70	0.4
Comparative Example 5	GI	None	J	70	0.4
Comparative Example 6	GI	None	K	70	0.4
Comparative Example 7	GI	None	L	70	0.4
Comparative Example 8	GI	None	M	70	0.4
Comparative Example 9	GI	None	N	70	0.4
Comparative Example 10	GI	Chemical Plating	I	70	0.4
Comparative Example 11	GI	Phosphate Conversion Coating	J	70	0.4

Table 2

Identifier	Coated Substrate Performance Ratings			
	Corrosion Resistance	Folding Adhesion		Coin Scratching
		Primary	Secondary	
Example 1	⊙	⊙	⊙	⊙ - O
Example 2	⊙ - O	⊙	⊙	⊙ - O
Example 3	⊙ - O	⊙	⊙	⊙ - O
Example 4	⊙ - O	⊙	⊙	⊙ - O
Example 5	⊙ - O	⊙	⊙	⊙ - O
Example 6	⊙	⊙	⊙	⊙ - O
Example 7	⊙ - O	⊙	⊙	⊙ - O
Example 8	⊙ - O	⊙	⊙	⊙ - O
Example 9	⊙	⊙	⊙	⊙ - O
Example 10	⊙	⊙	⊙	⊙ - O
Example 11	⊙	⊙	⊙ - O	⊙ - O
Example 12	⊙ - O	⊙	⊙	⊙
Example 13	⊙	⊙	⊙ - O	⊙
Comparative Example 1	X	X	X	X
Comparative Example 2	X	X	X	X
Comparative Example 3	X	X	X	X
Comparative Example 4	Δ	Δ	X	Δ
Comparative Example 5	X	X	X	X
Comparative Example 6	X	X	X	X
Comparative Example 7	Δ	X	X	X
Comparative Example 8	X	X	X	X
Comparative Example 9	X	X	X	X
Comparative Example 10	Δ	Δ	Δ	Δ
Comparative Example 11	Δ	Δ	Δ	Δ



- (I) forming a layer of a liquid composition according to claim 3 over at least one of a metallic surface of said metal substrate, a surface formed by chemical plating on a metallic surface of said metal substrate, and a phosphate conversion coating formed on a metallic surface of said metal substrate, said layer of said liquid composition having a non-volatiles content that is from 0.05 to 1.0 g/m<sup>2</sup>; and
  - (II) drying said layer of liquid composition, without removing any of said liquid by any other method than volatilization, to form a dry coating.
7. A process for making a coated metal substrate, said process comprising operations of:
  - (I) forming a layer of a liquid composition according to claim 2 over at least one of a metallic surface of said metal substrate, a surface formed by chemical plating on a metallic surface of said metal substrate, and a phosphate conversion coating formed on a metallic surface of said metal substrate, said layer of said liquid composition having a non-volatiles content that is from 0.05 to 1.0 g/m<sup>2</sup>; and
  - (II) drying said layer of liquid composition, without removing any of said liquid by any other method than volatilization, to form a dry coating.
8. A process for making a coated metal substrate, said process comprising operations of:
  - (I) forming a layer of a liquid composition according to claim 1 over at least one of a metallic surface of said metal substrate, a surface formed by chemical plating on a metallic surface of said metal substrate, and a phosphate conversion coating formed on a metallic surface of said metal substrate, said layer of said liquid composition having a non-volatiles content that is from 0.05 to 1.0 g/m<sup>2</sup>; and
  - (II) drying said layer of liquid composition, without removing any of said liquid by any other method than volatilization, to form a dry coating.
9. An article of manufacture comprising a coated metal surface formed by a process according to any one of claims 5 through 8.

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(57) Abstract: A chromium-free liquid treatment composition that contains (a) at least one resin selected from a group consisting of urethane resins, epoxy resins, and acrylic resins, (b) at least one silane coupling agent, and (c) dispersed solid particles with a mean particle diameter of 1  $\mu\text{m}$  or less provides a metallic surface, optionally already having a chemical plating or phosphate conversion coating, with superior corrosion resistance and paint adherence after subsequent painting. Of the non-volatiles content of the liquid treatment composition, (a) is 20 to 70 percent by weight, (b) is 10 to 60 percent by weight, and (c) is 10 to 40 percent by weight. This treatment composition is used by forming on the surface to be treated a liquid layer of the treatment composition that has a non-volatiles content of 0.05 to 1.0 g/m<sup>2</sup> and then drying the liquid layer into place on the surface to form the protective coating.

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UTILITY OR DESIGN  
PATENT APPLICATION**☐ Declaration Submitted with Initial Filing OR ☒ Declaration Submitted after Initial Filing

Attorney Docket Number

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First Named Inventor

Kinoshita, et al.

**COMPLETE IF KNOWN**

Application Number

Filing Date

Group Art Unit

Examiner Name

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**PRE-PAINT TREATMENT OF METAL AND PRODUCT THEREOF**

(Title of the Invention)

the specification of which

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY) **9/12/2000** as United States Application Number or PCT InternationalApplication Number **PCT/US/00/24930** and was amended on (MM/DD/YYYY) \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1.56.

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H11-258309	Japan	9/13/1999	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
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**DECLARATION****Page 2**

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U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)
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DECLARATION										ADDITIONAL INVENTOR(S) Supplemental Sheet									
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Residence: City			State			Country			Citizenship										
Post Office Address																			
Post Office Address																			
City			State			Zip			Country			Applicant Authority							
<b>Name of Additional Joint Inventor, if any:</b>										<input type="checkbox"/> A petition has been filed for this unsigned inventor									
Given Name			Middle Initial			Family Name			Suffix e.g. Jr.										
Inventor's Signature							Date												
Residence: City			State			Country			Citizenship										
Post Office Address																			
Post Office Address																			
City			State			Zip			Country			Applicant Authority							
<input type="checkbox"/> Additional inventors are being named on supplemental sheet(s) attached hereto																			